Synthesis and Structure of 9-Nitrosojulolidine

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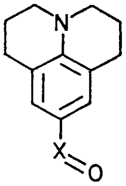
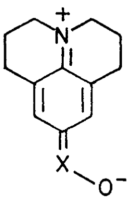
Summary A ^{1}H n.m.r. study of internal rotation in the hitherto unknown 9-nitrosojulolidine (I) yields $\Delta H\ddagger = 17{\cdot}1\,(\pm 1{\cdot}5)$ kcal mol^{-1} and $\Delta S\ddagger = 11{\cdot}6 \pm 6$ cal K^{-1} mol^{-1} for rotation of the nitroso-group; an appreciably lower resistance is found for the analogous formyl group rotation in isoelectronic 9-formyljulolidine (III), the corresponding activation parameters being $\Delta H\ddagger = 11{\cdot}9 \pm 1{\cdot}0$ kcal mol^{-1} and $\Delta S\ddagger = 3{\cdot}9 \pm 4$ cal K^{-1} mol^{-1}.



(I) X = N
(III) X = CH



(II) X = N
(IV) X = CH

IN 1892, Pinkus reported[1] an unsuccessful attempt to prepare 9-nitrosojulolidine (I). We now report that this elusive[1-3] compound, required in connection with a study of aromatic structure (*vide infra*) may be readily prepared by treatment of julolidine with excess of dry nitrosyl chloride in ether under nitrogen. Work-up by basification and ether extraction gave compound (I) as prisms with a steel blue lustre,† m.p. 163·5—164 °C.

† The crystals are green to transmitted daylight as expected (refs. 4 and 5) for the monomeric form (I); we have confirmed the monomeric nature of (I) in the crystal by an *X*-ray diffraction study. Compound (I) gives a satisfactory microanalysis.

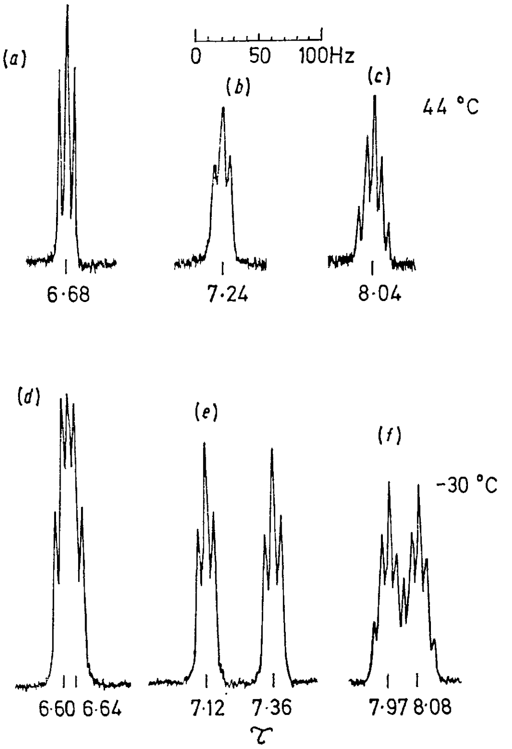
The monomeric nature of (I) in solution is indicated by its molecular weight and by the concentration insensitive $n \rightarrow \pi^*$ band of the nitroso-group.

Activation parameters for internal rotation

Compound		Solvent	T_c/°C^{a}	$\Delta H\ddagger$/kcal mol^{-1b}	$\Delta S\ddagger$/cal K^{-} mol^{-1b}	$\Delta G\ddagger$/kcal mol^{-1b}	Ref.
9-Nitrosojulolidine (I) ..	..	$CDCl_3$	29 ±4	17·1 ±1·5	11·6 ±6	14·2 ±0·2^{e}	
Nitrosobenzene	..	(vapour)		3·9 ±1^{c}			7
9-Formyljulolidine (III)^{d}	..	$CDCl_3$	−51 ±2	11·9 ±1·0	3·9 ±4	10·9 ±0·2^{e}	
Benzaldehyde	..	(vapour)		4·90 ±0·43^{c}			8
„	..	C_2H_3Cl	−123			7·9^{f}	9

[a] The coalescence temperature. [b] The activation parameters derived in the present work correspond to a transmission of unity. [c] Strictly corresponds to V_2 of the potential function $V = (V_2/2)(1-\cos 2\alpha)$; however the difference between V_2 and $\Delta H\ddagger$, the zero-point vibrational energy, is small and may be neglected for the present comparison. [d] Kinetic measurements for compound (III) were made at 100 MHz; the "frozen" spectrum corresponds to an AB system with ν_{AB} 25·8 Hz and J_{AB} 1·9 Hz. [e] At 250 K. [f] At 150 K.

At 44 °C, the 220 MHz ^1H n.m.r. spectrum of 9-nitrosojulolidine (I) (*ca.* 0·1M in $CDCl_3$) comprises a broadened aromatic resonance, centred near τ 2·7, and the methylene signals shown in the Figure. Lowering the temperature, which reduces the rate of rotation around the Ar–NO bond, produces a marked effect, and at −30 °C the aromatic protons correspond to an AB system with ν_{AB} 401 Hz and J_{AB} 2·2 Hz, while each of the three methylene resonances observed at high temperature now exhibits an additional splitting (Figure). The observation of chemically shifted positions, even from the methylene protons furthest from the nitroso-group, that is, the *syn*- and *anti*-CH_2–N protons, reflects the large magnetic anisotropy of the nitroso-function.[6] Spectral changes deriving from *conformational processes* of the trimethylene chains in (I) were not detected at temperatures down to −60 °C. By contrast with the behaviour observed for (I), the symmetrical compounds 9-nitrojulolidine‡ and julolidine itself show no temperature-dependent behaviour down to −60 °C.



220 MHz ^1H *n.m.r. spectra of the methylene resonances from* (a) CH_2–N, (b) Ar–CH_2, and (c) Ar–C–CH_2 *protons of* (I) *at* 44 °C: (d), (e), *and* (f) *are the corresponding resonances at* −30 °C (*which have chemical shift splittings of* 0·044, 0·241, *and* 0·108 *p.p.m. respectively*).

A kinetic analysis of the collapse of the aromatic AB system, rates being measured by matching experimental and computer-calculated spectra, gave the activation parameters for nitroso-group rotation (Table) along with those, measured similarly, for formyl group rotation in 9-formyljuloliodine[2] (III). Comparison of the enthalpies of activation for rotation in compounds (I) and (III) with the corresponding barriers for nitroso and formyl group rotation in nitrosobenzene and benzaldehyde shows that the quinolizidine unit functions, in a mesomeric sense, as an extremely effective electron-releasing group; the zwitterionic forms (II) and (IV) contribute substantially to the electronic structures of compounds (I) and (III). It is, however, noteworthy that nitrogen lone pair delocalisation in the ground state is appreciably better developed in 9-nitrosojulolidine than in its isoelectronic 9-formyl counterpart.[10]

We thank the S.R.C. for research studentships (to R.K.M. and R.D.)

(*Received, June 2nd,* 1971; *Com.* 891.)

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‡ The 9-nitro compound, m.p. 166—167 °C, (correct analysis obtained) was prepared in good yield by oxidation of compound (I) with *m*-chloroperbenzoic acid.

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